

Corrosion Inhibition of Acid-Treated Geothermal Brine – Results from Pilot Testing in Southern Negros, Philippines

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ABSTRACT

Corrosion inhibition testing of carbon steel pipe with acid-treated brine using chemical organic inhibitor was conducted at Nasuji Sector, Southern Negros Geothermal Production Field, Philippines. Brine at 160°C was acid treated to reduce the pH from ~7 to ~4.5 and then cooled to 120 °C to simulate temperature drop from a second flash system. The acid was introduced to effect pH modification of brine chemistry to delay polymerization of silica and/or prolong the induction time.

Corrosion rates were monitored using linear polarization measurement probes before and after addition of sulfuric acid. Weight-loss method of measuring corrosion rates was also used by installing metal coupons. The experiment was run for more than 30 days.

Corrosion inhibition of carbon steel with acid-treated brine using 10 ppm organic chemical inhibitor proved that it can substantially reduce corrosion rates.

1. INTRODUCTION

To generate more power, some high-temperature geothermal power plants are designed to run on Double-Flash Steam Power Cycles. This means that exit brine temperature from the second flash vessel could be as low as 120°C or lower. In most instances, brine after the second flash vessel will be supersaturated with silica. It is therefore imperative to find ways to prevent silica polymerization and eventual deposition in brine pipelines.

To prevent silica deposition in the re-injection system, one can use either organic silica inhibitor or pH modification technique to delay silica polymerization until brine reaches the wellbore formation. However, pH modification could induce corrosion problems along the line, as reducing pH could increase the corrosion rate and the probability of material failure. Organic silica inhibitor, on the other hand, is quite expensive.

In this study, the use of high temperature organic chemical corrosion inhibitor in carbon steel pipe with geothermal acid-treated brine is investigated. Sulfuric acid was added to the brine to affect pH-modification for delaying silica polymerization. The experiment was conducted at Nasuji Sector, Southern Negros Geothermal Production Field, Philippines. The typical selected chemistry of the Nasuji brine is given in Table 1.

2. EXPERIMENTAL SET-UP

The online field testing facility is a compartmentalized pipeline. The brine enters the first section of the pipeline

(blank or reference line condition) from the main re-injection line at ~ 160°C. Sulfuric acid is introduced before the second pipe section, dropping the pH to ~4.5. Water bath cooled the acid-treated brine to ~120°C before the third pipe section. Organic chemical corrosion inhibitor is then injected before the fourth pipe section.

Table 1 Nasuji Sector, SNGPF Selected Geothermal Brine Chemistry.

Parameter	Concentration, ppm
pH	7.34
SiO ₂	714
Fe	1
SO ₄	23
total CO ₂	21.75
H ₂ S	1.46

Linear polarization resistance probes were placed at the third pipe section (acid-treated brine at 120°C) and the second probe was placed after corrosion inhibitor injection.

Polished, cleaned and prior-weighed metal coupons were placed at each section to determine material loss due to corrosion.

Ten feet long two-inch diameter carbon steel pipe was used for each pipe section to ensure adequate mixing of the brine after the chemical is introduced. Temperature of each pipe section was maintained by insulating with abaca fiber.

The high temperature organic chemical corrosion inhibitor was injected at 10 ppm concentration. Temperature, pH and flow rates were monitored. The test was run for a month to achieve stable corrosion rates.

3. RESULTS AND DISCUSSIONS

The application of pH modification to delay silica polymerization or prolong its induction period was patterned after previous experiments in Malitbog Sector, Tongonan Leyte, Philippines (Alcober et.al., 2005) and polymerization test results from well PT-5D at Northern Negros, which indicated that a pH of 4.2 was sufficient to delay polymerization of excess silica.

Based on the results, however, silica deposition was observed in all of the weigh-loss metal coupons even in acid treated brine. The characteristics of the silica deposited in the acid treated brine is different from the untreated brine in that the latter deposits are hard, adherent and brittle whereas in the former the silica deposits are soft and can easily be removed. No viable material loss measurement can be established with these results. This suggested that colloidal silica is already present in the brine when it entered the field testing set-up. It also indicates that Nasuji geothermal brine has a very short induction period.

Petrological analysis (Rosell and Delfin, 2006) showed that deposits from metal coupons 1-3 harvested from the first pipe section (untreated brine $\sim 160^{\circ}\text{C}$) were identified as amorphous silica scales, relatively hard and adherent to the metal surface (Figure 1). Coupons 4 – 6 deposits (acid-treated, 160°C) are greenish gray in color, and very thin (Figure 2). Coupons 7-9 (acid-treated, 120°C) have thick whitish gray deposits (Figure 3). Coupons 10-12 have light brownish deposits covering most of the metal surface (Figure 4).

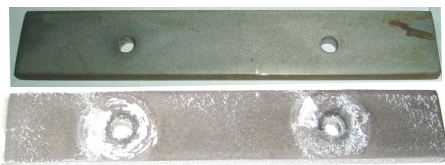


Figure 1: Metal coupon before (above) and after (below) the field testing experiment at the first pipe section, the untreated section with geothermal brine at $\sim 160^{\circ}\text{C}$

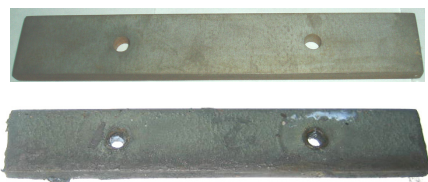


Figure 2: Metal coupon before (above) and after (below) the field testing experiment at the second pipe section, with acid-treated geothermal brine at $\sim 160^{\circ}\text{C}$



Figure 3: Metal coupon before (above) and after (below) the field testing experiment at the third pipe section, with acid-treated geothermal brine at $\sim 120^{\circ}\text{C}$



Figure 4: Metal coupon before (above) and after (below) the field testing experiment at the fourth pipe section, with acid-treated and organic chemical inhibitor injected geothermal brine at $\sim 120^{\circ}\text{C}$

To study the corrosion potential of the geothermal brine upon addition of sulfuric acid and cooling, Pourbaix diagrams were constructed to show the effect of pH and cooling. At the natural state of the brine at 160°C , it is somewhat protected by the passivity action of Fe_2S_3 . Lowering the pH to 4.5, however, will bring the redox

reaction to dissolution of iron metal (Figure 5). At lower temperature (120°C), the redox reaction still favors the dissolution of iron metal (Figure 6).

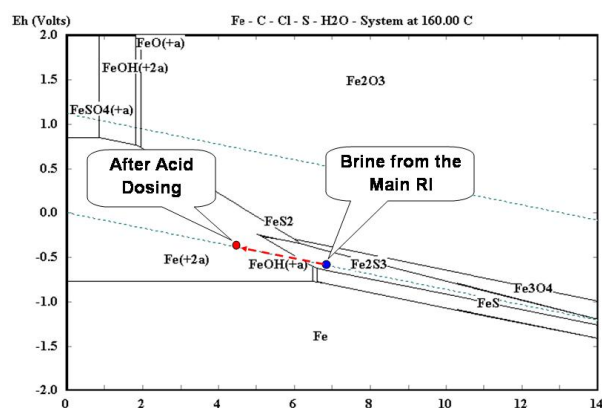


Figure 5: Pourbaix diagram of Nasuji geothermal brine at 160°C

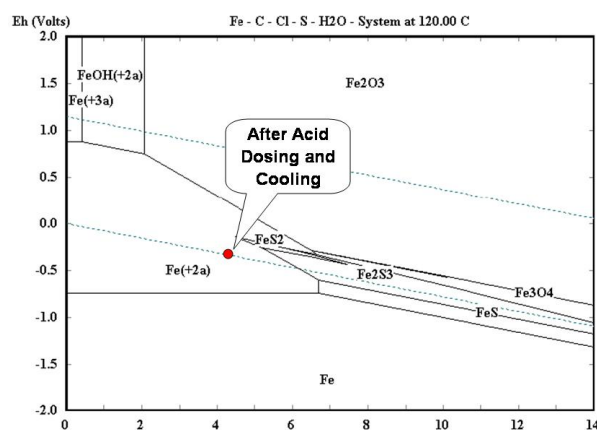


Figure 6: Pourbaix diagram of Nasuji geothermal brine at 120°C

A speciation program was used to simulate the effect of sulfuric acid addition to Nasuji geothermal brine. Lowering the pH to 4.5 has no significant effect on saturation indices of amorphous silica both in gel and precipitate form (Figure 7). This means that, on the basis of thermodynamics, formation of amorphous silica gel and precipitates cannot be prevented at target pH of 4.5 but the amount will be controlled by kinetics, induction time, seeding, etc. Baumann (1959) first observed that at certain conditions of pH (5.8 to 9) and silica concentration, there is an “induction period” during which there is little or no polymerization of monomer. Induction phenomenon can also be considered in terms of nucleation of colloidal particles (Iler, 1978). The combination of metal ion with silicic acid may be regarded as an adsorption of metal hydroxide on the silica. Combination does not occur much below the pH at which the metal hydroxide would be formed. It is possible therefore, especially at low pH, that the combination between silicic acid and metal ion involves the association of polymeric units both of silica and of basic metal cations forming chelate-like bonding (Iler, 1978). This chelate-like bonding of colloidal silica with metal ions in the brine can explain the observed amorphous silica precipitates in metal coupons 4 – 12. This can also explain why the amorphous silica formed in metal coupons 4 – 12 is loosely attached; the bonding sites of the colloidal silica were reduced due to adsorbed metal ions. The different coloration of the metal

coupons is due to the preferred metal ions adsorbed at different conditions. The brownish coloration of metal coupons 10–12 can also be attributed to adsorbed organic polymer from the injected corrosion inhibitor.

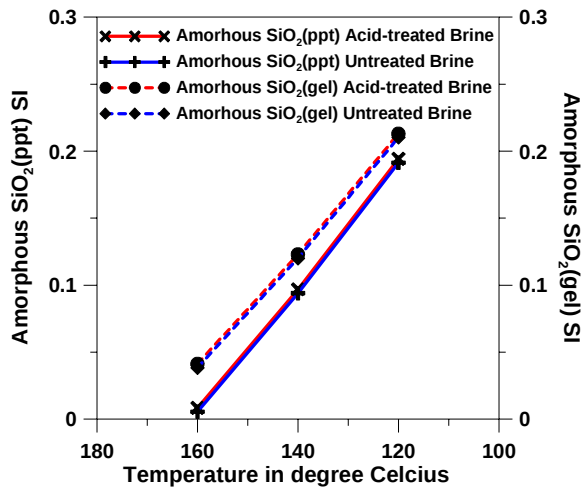


Figure 7: Saturation of Amorphous SiO₂ (gel and precipitate form) at untreated and acid-treated geothermal brine

Magnetite and hematite saturation indices are shown in Figure 8. Saturation index of hematite was slightly lowered upon addition of sulfuric acid but has the same general increasing trend with untreated brine upon cooling. Acid-treated brine showed decreasing saturation indices of magnetite on cooling. Magnetite saturation of untreated brine showed increasing trend on cooling. However, looking back at the Pourbaix diagrams, hematite and magnetite will not form at pH 4.5. Formation and passivity of iron sulfides has the real probability of protecting carbon steel pipe at pH 4.5.

Pyrite saturation indices and pH of acid-treated and untreated brine are shown in Figure 9. The pH of untreated brine is about 6.4 and for the acid-treated brine the pH is 4.4. The target pH of 4.5 is measured at ambient temperature.

Untreated brine is slightly undersaturated with respect to pyrite but cooling increases the saturation and become supersaturated at 120°C. Addition of sulfuric acid to lower the pH decreases the saturation of pyrite and cooling decreases it further logarithmically, offering no protection against corrosion of carbon steel.

The measured corrosion rates based on the linear polarization resistance (LPR) measurements are shown in Figure 10. The measured stable corrosion rate of LPR probe on acid-treated brine without inhibitor is ~0.12 mm/year towards the end of experiment. In comparison, the corrosion rate registered towards the end of the experiment from acid-treated brine with inhibitor is just ~0.02 mm/year. This represents ~80% reduction due to 10 ppm concentration organic chemical corrosion inhibitor.

The design corrosion rate allowance for carbon steel pipe is ~0.12 mm/year. It shows that even the acid-treated brine without inhibitor would be just at the limit of the corrosion allowance which is unacceptable because the low pH will cause dissolution of iron metal based on the Pourbaix diagrams. This can be explained by the fact that amorphous

silica precipitate deposited and covered the metal surface thus acted as a barrier against corrosive attacked of the acidic fluid. The loosely bound precipitates, however, can be stripped by turbulent flow and therefore no real long term protection can be expected.

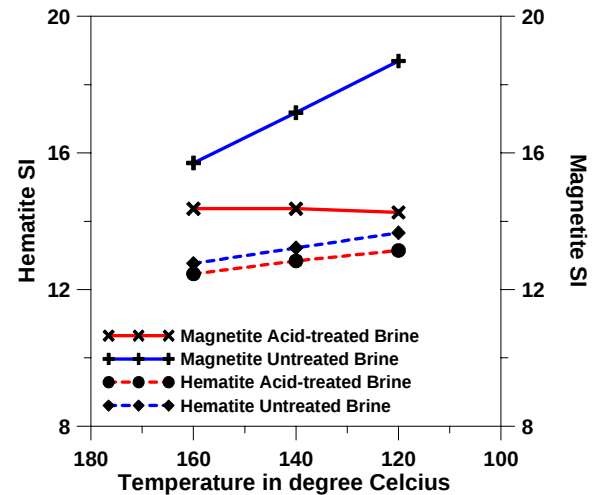


Figure 8: Magnetite and hematite saturation indices of acid-treated and untreated Nasuji geothermal brine

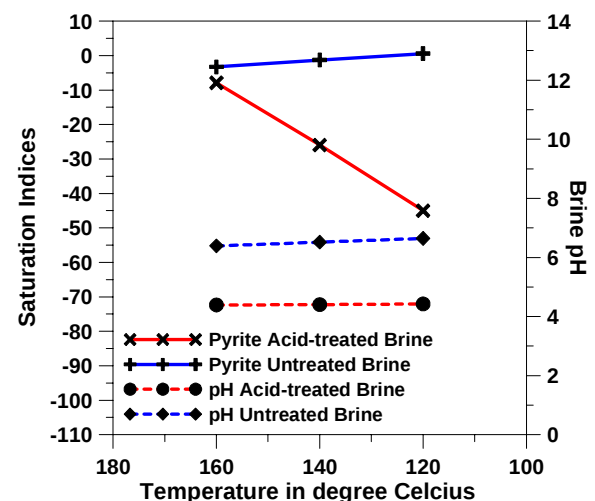


Figure 9: Saturation indices of pyrite and pH of acid-treated and untreated Nasuji geothermal brine

CONCLUSIONS

A field experiment was conducted for combined pH modification silica inhibition and organic chemical corrosion inhibition at Nasuji Sector, SNGPF Philippines. Sulfuric acid was added to lower the pH to 4.5 and organic chemical inhibitor was injected to prevent corrosion.

The results of the experiments indicated that colloidal silica was already present in the brine when it entered the experimental set-up. Amorphous silica formed hard and adherent deposits on the untreated section of the test set-up. Soft and loosely bound silica precipitate deposited on the metal surface at pipe sections with acid-treated brine. These deposits acted as a barrier against corrosive attacked of the acidic fluid.

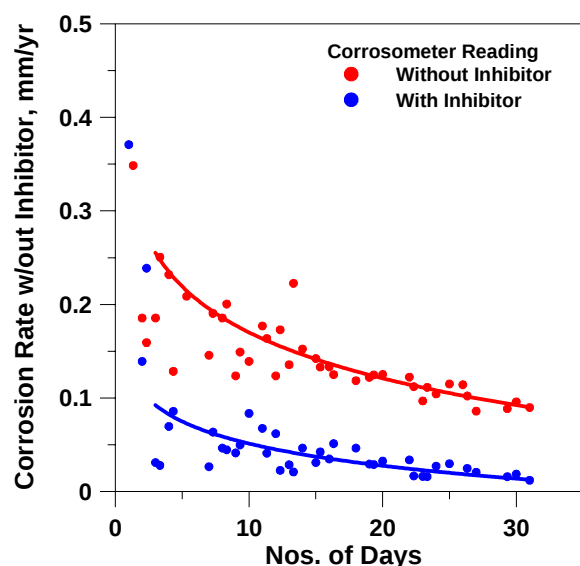


Figure 10: Corrosion rates of LPR probes on acid-treated geothermal brine with and without organic chemical corrosion inhibitor

The measured corrosion rates from linear polarization measurements are ~ 0.12 mm/year for acid-treated brine without corrosion inhibitor and ~ 0.02 mm/year with inhibitor. This represents 80% reduction on corrosion due to the corrosion inhibitor. The actual inhibition efficiency of the chemical inhibitor, however, can not be established since amorphous silica precipitates covered the metal surface and also acted as barrier against corrosive attack of acidic fluid.

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